

Tuning of Ziegler Natta Catalyst using Emulsion Technique

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Abstract

The present paper studies emulsion technique to reform the catalyst morphology, from granular to regular with the novel organomagnesium precursor, $\{Mg(OR')X\}.a\{MgX_2\}.b\{Mg(OR')_2\}.c\{R'OH\}$. Various work parameters were studied and found to be affecting catalyst activity and morphology. Uniform PSD and improved BD of polymer reflected the change from granular to regular morphology.

Keywords: Catalysts; Polymer; Morphology; Ziegler Natta; Organomagnesium

Introduction

Ziegler Natta polyolefin catalysts (ZN catalysts) are used to produce large volumes of polypropylene and polyethylene [1-4]. They are usually comprised of a titanium halide supported on magnesium compound with an organic compound known as an internal electron donor and support both regulates the morphology of catalyst [5,6], that play a vital role in manufacturing process of polymer, since it controls the molecular architecture of the final product [7-8]. Therefore polymer takes on shape and morphology of solid component of Ziegler Natta catalyst system which have characteristics influence on polymer properties such as bulk density, flow ability, particle adhesion etc [9]. Precipitated and supported catalysts represent the majority of Ziegler Natta catalyst for olefins. Precipitated ZN catalyst involves the precipitation of catalyst at higher temperature from solution of magnesium based compound and internal donor in presence of large amount of aliphatic hydrocarbon [10-14]. It is difficult to carry out precipitation in controlled and reproducible manner,

leading to the unsatisfactory morphology of precipitated catalyst particles. Another drawback associated with precipitation process is tar like intermediate gets agglomerate and sticks to the wall of reactor, and further to the loss of the morphology of the catalyst [15,16]. To carry out steady and smooth operations during polymerization with effects on thermal & chemical properties of polymer [17-20], it's crucial to make polymers from spherical particles. Therefore ideal supports provide catalysts with high activity for the production of polyolefin. Various methods have been reported for producing support for Ziegler Natta catalyst such as ball milling [21-25], melt quenching [26], seeding process [27], spray drying [28-31] and emulsion [32,33,34,35].

The ball-milling method allows reducing the size of $MgCl_2$ crystallites, as a consequence increasing the surface area of the catalyst and its activity. However, rampant morphology is the major disadvantage of this process.

Spray drying technique provides an opportunity to control the particle size of an inorganic support and a supported catalyst, which in turn is used to control the particle size and polymer properties. It's an alternative to impregnating the catalyst on a support and can be applied either directly to prepare spherical particles of catalyst or to prepare the porous particles of support derived from the magnesium dichloride and alcohols.

ZN catalyst prepared via emulsification-solidification method involves in situ generation of internal donor during catalyst synthesis as well as the formation of liquid/liquid two phase system in which one phase is solution of the catalysts components in an inert solvent. Droplets of dispersed phase of emulsion get solidified at higher temperature to form solid catalysts component. Additional examples of emulsion or controlled precipitation can be seen in the work of BASF, Borealis [36-38] and Shell. Ziegler Natta catalysts prepared using emulsion system has compact, spherical particles with good intra particle homogeneity. The polymer particles produced with these types of catalyst are compact and spherical with a narrow particle size distribution.

In this paper, emulsion technique was explored to reform the catalyst morphology from granular to regular with the novel organomagnesium precursor, having formula $\{Mg(OR')X\}_a\{MgX_2\}_b\{Mg(OR')_2\}_c\{R'OH\}$ where a:b:c is in range of 0.1-99.8 : 0.1-99.8 : 0.1-99.8 [39].

Viscoplex, an emulsion stabilizer was used to provide sphericity and inhibit aggregation of catalyst particles. The morphology of catalyst was regular with uniform particle size distribution which is confirmed by SEM. Factors influencing the catalyst properties and activity were also investigated. The resultant catalyst, in association with an alkyl aluminum cocatalyst and an external donor was effective in slurry polymerization of propylene. The polymer particles produced were replica of the catalyst particles and improved morphology was also reflected through bulk density of polypropylene (BD~ 0.38 to 0.43 g/cc).

Experimental Section

Materials

All operations were carried out using standard Schlenk line techniques under dry nitrogen atmosphere unless otherwise stated. n-Hexane (Merck) was purified by distillation with Na metal/benzophenone. $TiCl_4$ (Merck) was purified by distillation. Chlorobenzene (Rankem) was dried with 3Å molecular sieves. Cyclohexyl

methyl dimethoxysilane (CHMDMS; C-donor) was received from Aldrich and used as such. Triethyl aluminum (TEAL) from M/s Gulbrandsen Chemicals was used as received. Diisobutyl phthalate (99%, Sigma-Aldrich) was distilled before use. Viscoplex®1-254 was used as received from M/s Evonik Industries. High purity nitrogen was used for the handling of all compounds. All the liquid compounds were deoxygenated before use.

Instrumentation

Titanium content in the catalyst was determined by dissolving the solid in an acidic media afterward; all of the titanium contained in the catalysts was converted into Ti^{4+} by addition of H_2O_2 . UV-Vis spectra of the resultant solution of peroxotitanium complexes were recorded on a Perkin-Elmer UV Lambda 35 spectrometer. The intensity of a peak at 417 nm ($\epsilon = 782.7 \text{ L}^{-1} \text{ mol}^{-1} \text{ cm}^{-1}$) was used to quantify the titanium content. SEM images were acquired using a JEOL, (JSM-6610 LV Model) at room temperature at accelerating voltage of 5 kV. The samples were prepared in glove box to prevent oxidation. The samples were immediately transferred in SEM chamber under nitrogen atmosphere and examined by SEM at 5 kV. Average particle size and particle size distribution (PSD) data for catalyst was obtained from Cilas 1190 Laser Particle Size Analyzer. The sample was prepared in paraffin oil (33.5 cSt) under inert atmosphere and immediately transferred to analyzer. The vibratory sieve shaker (Analysette 3 model) from FRITTSCH, Germany was used to determine the particle size distribution of polypropylene.

Preparation of Organomagnesium Precursor

The synthesis procedure was used as described in WO/2014/045259 without any variation. 2.4. Preparation of catalyst system. To 220 ml (2.0mole) of $TiCl_4$ solution maintained at desired temperature, added 100 ml of organomagnesium precursor (Mg = 1.1 wt%) along with 2.0 ml of Viscoplex ® (1-254). The emulsion formed was heated to 70°C. A solution of DIBP (0.006 mole in 10 ml toluene) was added over a period of 10 min. The reaction temperature was increased to 110°C in 10 min and maintained for 0.5 h. After settling and decantation, the suspended solid was again treated with 120 ml $TiCl_4$ /chlorobenzene (50/50 v/v) and the mixture was maintained under stirring for 15 min at 110°C. After settling and decanting, the solid underwent washing with 80 ml chlorobenzene at 110°C followed by washing with hexane (100 × 4 ml) at 65°C. Finally the solid catalyst was dried under hot nitrogen till freely flowing.

Slurry Polymerization of Propylene

Propylene polymerization was carried out in 1L Buchi reactor which was previously conditioned under nitrogen. The reactor was charged with 250 ml of dry hexane containing 0.5 ml of solution of 10 wt% triethylaluminum followed by 100 ml of dry hexane containing calculated amount of 10 wt % solution of triethylaluminum and 5 wt% solution of cyclohexyl methyl dimethoxysilane and weighed amount of catalyst. The reactor was pressurized with hydrogen to 5 ml @ 1bar then charged with 5 kg/cm³ of propylene under stirring at 750 rpm. The reactor was heated to and then held at 70°C for 2 hrs. At the end, the reactor was vented and the polymer was recovered at ambient conditions.

Results and Discussion

A novel organomagnesium precursor having formula $\{Mg(OR')X\}_a\{MgX_2\}_b\{Mg(OR')_2\}_c\{R'OH\}$ where a:b:c is in range of 0.1-99.8 : 0.1-99.8 : 0.1- 99.8) was prepared by contacting magnesium metal with organohalide and alcohol in presence of the solvent. The organomagnesium precursor's efficacy was established by utilizing as a support to prepare Ziegler Natta catalyst. The liquid to solid phase transition resulted in catalyst having high activity and regular morphology of the polymer.

The morphology of catalyst is one of the crucial factors in Ziegler-Natta chemistry. It is desirable to have regular catalyst hence the polymer which is enlarged reflection of the catalyst, will be regular leading to manufacturing and processing benefits. It is always beneficial that the starting material i.e. the support itself is regular in nature hence various approaches are well known in Ziegler chemistry to obtain it. Solid to solid transition, emulsification & quenching followed by solidification & crystallization at higher temperature all these methods are used to get regular support for catalyst. Generally single entity of magnesium is used to synthesize ZN catalyst through solid to solid transition but the organomagnesium precursor, complex of different entities and the fact that it is liquid in its present form, is yet to be explored for Ziegler Natta catalyst.

Hence exploring emulsion based technique for obtaining regular catalyst as well as polymer using organomagnesium precursor was a challenge. For this purpose, Viscoplex was used as an emulsion stabilizer.

Ziegler Natta Catalyst was synthesized by the process where organomagnesium precursor is converted to active MgCl₂ matrix acting as a support in presence of Viscoplex as an emulsifier to attach transition metal as well as internal electron donor. The following methodology was adopted for the catalyst synthesis:

Emulsion formation at room temperature by the process where organomagnesium precursor is contacted with transition metal halide in presence of Viscoplex.

- Addition of phthalate based internal donor to this emulsion at higher temperature to get desired solid catalyst component.
- Recovery of the olefin polymerization catalyst component from the said solution.

The parameters which will be affecting the property of catalyst and catalytic activity in the polymerization of polypropylene were investigated.

Effect of ID/Mg Molar Ratio

Foremost focused was on catalyst activity so that sufficient amount of polymer is obtained for analysis. Since internal donor (ID) is known to play a dominant role in controlling the catalyst activity therefore the effect of ID/Mg molar ratio on catalyst activity was studied. The internal donor used here is diisobutyl phthalate (DIBP). It was added at different ID/Mg molar ratios (0.1, 0.15 and 0.25) for synthesizing catalysts. Table 1 shows the details of this study. At ID/Mg mol ratio of 0.10, the productivity of the catalyst is low as sufficient amount of internal donor is not present to produce active MgCl₂ sites. For ID/Mg mol ratio from 0.15 to 0.25, the activity of the catalyst decreased with increase in the DIBP amount. This can be explained by the fact that excess of internal donor prevents TiCl₄ coordination on MgCl₂ crystal faces by occupying some of the active sites on MgCl₂ support and hence decreases the activity of catalyst [40]. Therefore, the ratio of 0.15 for ID/Mg resulted in catalyst (ZN#635) has high activity with regular morphology of the polymer.

Catalyst	ID/Mg molar ratio	DIBP (ml)	Mg (wt%)	Ti (wt%)	Ester (wt%)	Productivity (kgPP/gcat)	Isotacticity (%)
ZN#1	0.1	1.1	15.2	5.5	15.4	3.8	90.2
ZN#2	0.15	1.7	16.6	3.3	18.6	5.4	90.4
ZN#3	0.25	3.3	11.4	7.5	22.2	3.2	95.2

Table 1: Catalytic activity at different ID/Mg molar ratio.

Effect of Ti/Mg Molar Ratio

The chlorination as well as titanation (fixing of transition metal onto the MgCl₂ matrix) step is carried out using TiCl₄ at different Ti/Mg molar ratios (35, 70 & 90) with optimized ID/Mg molar ratio of 0.15. Table 2 shows the details of the study. When the Ti/Mg molar ratio was increased from 35 to 70, Ti content fixed on the

MgCl₂ matrix leads to formation of more active sites and therefore one observes the increase in catalyst activity. But as this molar ratio further increases, the competition between DIBP and Ti for the active sites becomes more prominent resulting in the decrease in the titanium content of the catalyst and hence reduction in catalyst performance as shown in Figure 1.

Catalyst	Ti/Mg molar ratio	DIBP (ml)	Mg (wt%)	Ti (wt%)	Ester (wt%)	Productivity (kgPP/gcat)	Isotacticity (%)
ZN#4	35	1.7	16.8	2.5	20.9	3.4	93.1
ZN#5	70	1.7	16.3	3	20.9	5.1	93.5
ZN#6	90	1.7	16.5	2.7	21.3	3.9	94

Table 2: Catalytic activity at different ID/Mg molar ratio.

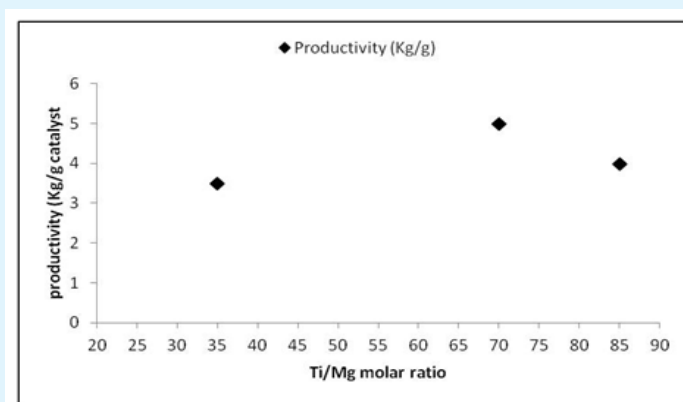


Figure 1: Activity profile of Ziegler Natta catalyst with variation in Ti/Mg molar ratio. Polymerization was performed at 5 bar propylene pressure and 70°C.

Effect of ID addition at Different Temperatures

Variation of DIBP addition at different temperature on catalyst activity as well as morphology was studied. Under optimized conditions, DIBP was added at temperature - 5°C, 25°C, 50°C and 70°C respectively and results are

shown in Table 3. It was found that addition of DIBP at higher temperature significantly increases the catalyst activity with maximum activity at 70°C. Effect of addition temperature on catalyst activity is shown in Figure 2.

Catalyst	Temp. (°C)	DIBP (ml)	Mg (wt%)	Ti (wt%)	Ester (wt%)	Productivity (kgPP/gcat)	Isotacticity (%)
ZN#7	-5	1.7	17.2	2.9	17.8	3.5	90.1
ZN#8	25	1.7	17.1	2.8	18.6	2.7	90.2
ZN#9	50	1.7	17.3	3.2	16.3	3.3	90
ZN#10	70	1.7	16.3	3	20.9	5	93.5

Table 3: Effect of DIBP addition at different temperature on catalytic activity.

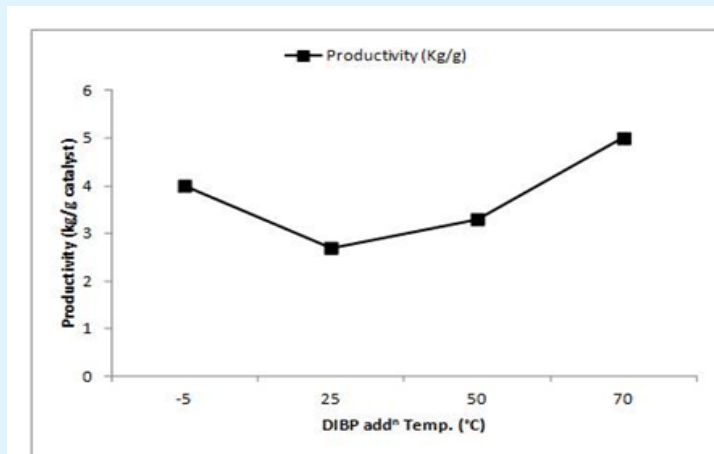


Figure 2: Activity profile of Ziegler Natta catalyst with variation of DIBP addition temperature. Polymerization was performed at 5 bar propylene pressure and 70°C.

Effect of Methodology of ID Addition

The morphology of the catalyst is best studied by particle size distribution where the distribution span is a measure of morphology control. The distribution span as defined by the following formula

$$\text{Span} = D90 - D10 / D50.$$

Where, D10 is the diameter at which 10% of the sample's mass is comprised of particles with a diameter less than this value.

D50 is the diameter of the particle that 50% of a sample's mass is smaller than and 50% of a sample's mass is larger than.

D90 is the diameter of the particle that 90% of a sample's mass comprised of particles with a diameter less than this value.

Table 4 shows span and the resultant bulk density of polymer. The narrow Span of the catalyst particle is indeed reflects in the resultant polymer property i.e bulk density which reaches > 0.4 g/cc hence indicating uniform morphology of the catalyst as well as polymer particle.

Catalyst	DIBP addn temp (°C)	Mg (wt%)	Ti (wt%)	Span	BD (g/cc)
ZN#7	-5	17.2	2.9	2.3	0.34
ZN#8	25	17.1	2.8	2.2	0.34
ZN#9	50	17.3	3.2	1.8	0.38
ZN#10	70	16.3	3	1.6	0.4

Table 4: The effect of addition of DIBP at different temperature on catalyst properties.

DIBP is known to affect the catalyst particle size and consecutively the morphology [41]. Hence it was decided to understand this aspect during catalyst synthesis using Viscoplex. The addition of DIBP was carried out firstly, using glass syringe with metal Luer lock and secondly, through syringe pump. In order to have uniformity, the syringes used were of same volumes.

Figure 3 shows the SEM micrograph of the two catalysts prepared through the discussed methodology. ZN#2 which was prepared by addition of DIBP through syringe pump has better morphology in comparison to ZN#5 prepared by adding DIBP directly through syringe.

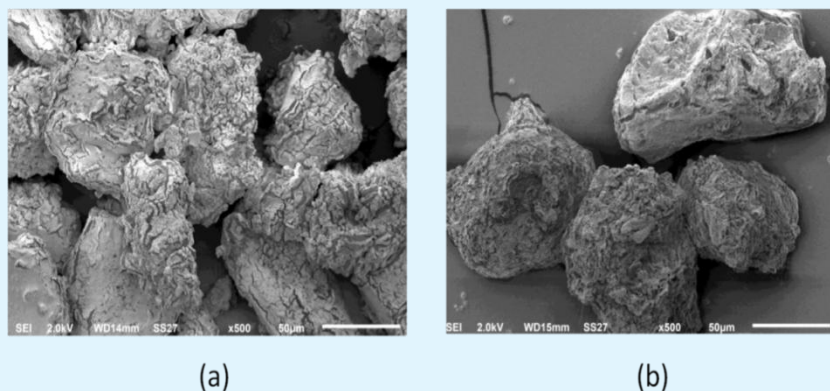


Figure 3: SEM micrographs of a) ZN#5 b) ZN#2

Effect of Holding Time after ID Addition

Another aspect of the catalyst synthesis which could have affected the morphology was holding time after the addition of DIBP. Hence under optimized reaction

conditions, after the addition of DIBP, the reaction mixture was stirred at 70°C with variation in holding time (0, 30 and 60 min). The effect of this study on the catalyst activity and morphology is tabulated in Table 5.

Catalyst	Holding time (min)	Mg (wt%)	Ti (wt%)	Ester (wt%)	Productivity (kgPP/gcat)	Isotacticity (%)	BD (g/cc)	Span
ZN#2	0	16.6	3.3	18.6	5.4	90.4	0.42	1.2
ZN#11	30	15.8	2.9	23.2	4	95.5	0.34	1.8
ZN#12	60	16	2.6	23.6	3.5	95.5	0.31	2

Table 5: Catalytic activity at different holding time after the addition of DIBP.

It was found that catalyst activity decreased with increase in holding time which might be because of the

replacement of $TiCl_4$ onto the $MgCl_2$ matrix by the bi-dentate nature of DIBP.

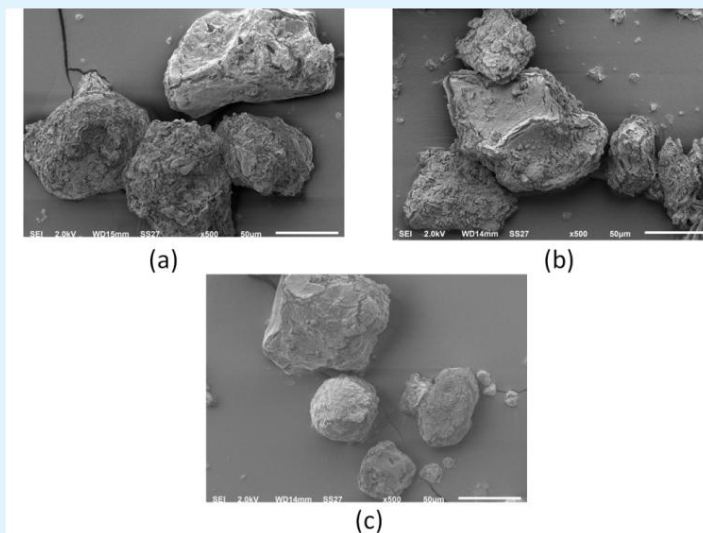


Figure 4: SEM micrograph of catalyst at different holding time a) ZN#2 (0 min) b) ZN#1 (30 min) c) ZN#12 (60 min).

The morphology of the three catalysts depicted the effect of holding time after DIBP addition as in Figure 4 SEM micrographs. ZN#2 where the holding time is 0 min, the catalyst morphology is almost regular while the other two catalysts have regular morphology with rough surfaces.

Effect of Washing on Catalyst Performance

After titanation, washing of the solid particulate product is very important to improve the catalyst activity

and morphology as these side products leads to agglomeration of the catalyst particles and hence spoils the shape of the catalyst. For this purpose, the solid particulate was washed with aromatic hydrocarbon i.e chlorobenzene (ClBz) at 110°C. Results are shown in Table 6. It was found that the activity of catalyst washed with aromatic hydrocarbon (ZN#13), was significantly improved than that of unwashed catalysts ZN#2 whereas the morphology was similar as shown in Figure 5.

Catalyst	Ti/Mg molar ratio	ClBz (ml)	Mg (wt%)	Ti (wt%)	Productivity (kg PP/gcat)	Isotacticity (%)	BD (g/cc)	Span
ZN#2	80	0	16.6	3.3	5.4	90.4	0.42	1.2
ZN#13	80	80	14.3	4.5	6.5	95.4	0.44	1.2

Table 6: Catalytic activity after washing with aromatic hydrocarbon at higher temperature.

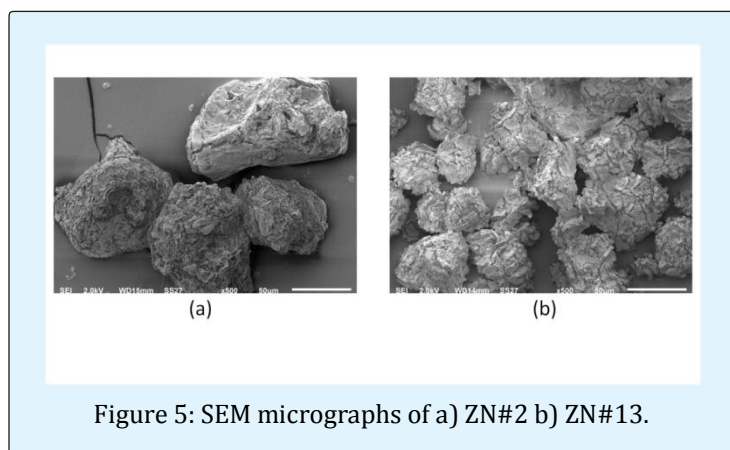


Figure 5: SEM micrographs of a) ZN#2 b) ZN#13.

Effect of Viscoplex as an Emulsifier

Viscoplex is used as an emulsifier in the proposed recipe of catalyst synthesis. It is not only crucial for stabilizing the emulsion, produced by the contact of liquid precursor with transition metal at 25°C but also have impact on catalyst activity and morphology. Since two

phases naturally tend to separate into a lower, denser phase and supernatant light phase, it is necessary to maintain the reaction product as an emulsion by agitation in the presence of an emulsion stabilizer. Table 7 shows the effect of variation in Viscoplex amount on catalyst activity under optimized reaction conditions

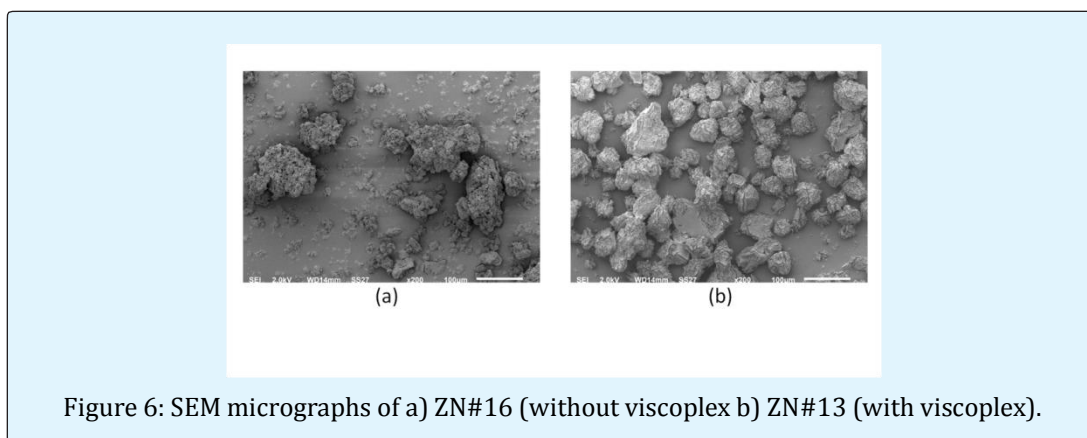
Catalyst	Viscoplex (ml)	Mg (wt%)	Ti (wt%)	Ester (wt%)	Productivity (kgPP/gcat)	BD (g/cc)	Span
ZN#14	1	16.8	3.3	17.8	2.4	0.4	2.7
ZN#13	2	14.3	4.5	22.7	6.5	0.44	1.3
ZN#15	4	13.3	3.3	31.2	catalyst inactive for polymerization		

Table 7: The effect of amount of Viscoplex on catalyst performance.

Figure 6 shows the SEM micrographs of the catalyst prepared using Viscoplex (ZN#13). Viscoplex as an emulsion stabilizer covers the catalyst support with thin

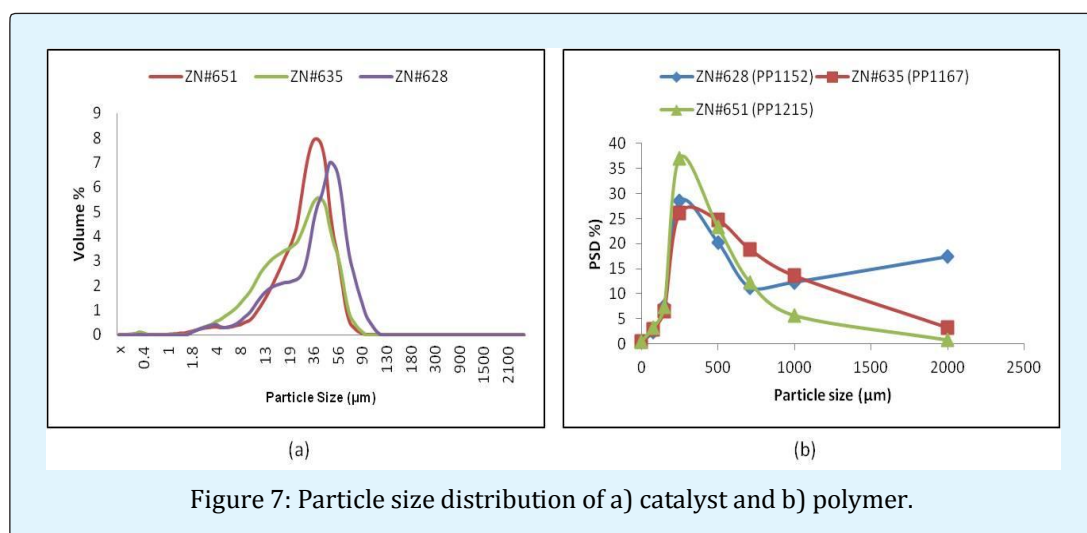
layer and protects it from cluster & breaking thereby protects its morphology resulting in regular catalyst without viscoplex have regular morphology with rough

surfaces while with Viscoplex morphology turns from regular to almost regular as shown in Figure 6.



Polymer particles produced in the polymerization replicated the morphology of catalyst particles as shown in Figure 7 where the particle size distributions of the

catalyst and polymer particles were observed to be very similar.



Conclusions

Ziegler Natta catalyst prepared via emulsion process using a novel organomagnesium precursor $\{Mg(OR)X\}$.a $\{MgX_2\}$.b $\{Mg(OR)2\}$.c $\{R'OH\}$, shows regular morphology as studied by SEM with uniform particle size distribution. Various work parameters were studied and it was verified that electron donor addition, holding time along with improvised washing step provided catalyst with high activity and good morphology. The resultant catalyst is effective in slurry polymerization of propylene, with uniform particle size distribution reflected in bulk density of polymer (BD >40 g/cc).

References

1. Steinborn D (2012) Fundamentals of Organometallic Catalysis. WileyVCH, Weinheim, Germany.
2. Kashiwa N (2004) The discovery and progress of $MgCl_2$ -supported $TiCl_4$ catalysts. Journal of Polymer Science Part A: Polymer Chemistry 42(1): 1-8.
3. Galli P, Vecellio G (2001) Technology: Driving force behind innovation and growth of polyolefins. Progress in Polymer Science 26(8): 1287-1336.

4. Vaughan A, Davis DS, Hagadorn JR (2012) Industrial catalysts for alkene polymerization. *Polymer Science: A Comprehensive Reference* 3: 657-672.
5. Makwana U, Naik DG, Singh G, Patel V, Patil HR, et al. (2009) Nature of phthalates as internal donors in high performance $MgCl_2$ supported titanium catalysts. *Catalysis Letters* 131(3-4): 624-631.
6. Kaur S, Singh G, Makwana U, Gupta VK (2009) Immobilization of Titanium Tetrachloride on Mixed Support of $MgCl_2 \cdot xEB$ /Poly(methyl acrylate-co-1-octene): Catalyst for Synthesis of Broad MWD Polyethylene. *Catalysis Letters* 132(1-2): 87-93.
7. Forte MC, Coutinho FMB (1996) Highly active magnesium chloride supported Ziegler-Natta catalysts with controlled morphology. *European Polymer Journal* 32(2): 223-231.
8. Arabi H, Abedini H, Dolatshahi H, Nejabat G (2013) Ziegler-Natta Catalyst Preparation Process: Influential Parameters on Particles Morphology and Activity of Catalyst in Propylene Polymerization. *Iranian Journal of Polymer Science and Technology* 26(3): 209-219.
9. Chadwick JC, Miedema A, Ruisch BJ, Sudmeijer O (1992) Effects of procatalyst composition on the stereospecificity of a Ziegler-Natta catalyst system. *Macromolecular Chemistry and Physics* 193(6): 1463-1468.
10. Ye ZY, Wang L, Feng LF, Gu XP, Chen HH, et al. (2002) Novel spherical Ziegler-Natta catalyst for polymerization and copolymerization. I. Spherical $MgCl_2$ support. *Journal of Polymer Science Part A: Polymer Chemistry* 40(18): 3112-3119.
11. Sozzani P, Bracco S, Comotti A, Simonutti R, Camurati I (2003) Stoichiometric compounds of magnesium dichloride with ethanol for the supported Ziegler-Natta catalysis: First recognition and multidimensional MAS NMR study. *Journal of the American Chemical Society* 125(42): 12881-12893.
12. Xu R, Liu D, Wang S, Wang N, Mao B (2007) Preparation of spherical $MgCl_2$ -supported bis(phenoxy-imine) zirconium complex for ethylene polymerization. *Journal of Molecular Catalysis A: Chemical* 263(1-2): 86-92.
13. Guan Z, Zheng Y, Jiao S (2002) Spherical $MgCl_2$ -supported MAO pre-catalysts: preparation, characterization and activity in ethylene polymerization. *Journal of Molecular Catalysis A: Chemical* 188(1-2): 123-131.
14. Parada A, Rajmankina T, Chirinos JJ, Morillo A (2002) Influence of support recrystallization techniques on catalyst performance in olefin polymerization. *European Polymer Journal* 38(10): 2093-2099.
15. Noristi L, Marchetti E, Baruzzi G, Sgarzi P (1994) Investigation on the particle growth mechanism in propylene polymerization with $MgCl_2$ -supported Ziegler-Natta catalysts. *Journal of Polymer Science Part A: Polymer Chemistry* 32(16): 3047-3059.
16. Abboud M, Denifl P, Reichert KH (2005) Fragmentation of Ziegler-Natta catalyst particles during propylene polymerization. *Macromolecular Materials and Engineering* 290(6): 558-564.
17. Parvez MA, Rahaman M, Suleiman MA, Soares JBP, Hussein IA (2014) Correlation of Polymerization Conditions with Thermal and Mechanical Properties of Polyethylenes Made with Ziegler-Natta Catalysts. *International Journal of Polymer Science* 2014: 1-10.
18. Aigner P, Paulik C, Krallis A, Kanellopoulos V (2016) Optimal Catalyst and Cocatalyst Precontacting in Industrial Ethylene Copolymerization Processes. *Journal of Polymers* 2016: 1-10.
19. Rahaman M, Parvez MA, Soares JBP, Hussein IA (2014) Effect of Polymerization Conditions on Thermal and Mechanical Properties of Ethylene/1-Butene Copolymer Made with Ziegler-Natta Catalysts. *International Journal of Polymer Science* 2014: 1-10.
20. Belmontes FA, Ramos-deValle LF, Espinoza-Martínez AB, Martínez-Colunga JG, Ramírez-Vargas E, et al. (2016) Effect of Different Nucleating Agents on the Crystallization of Ziegler-Natta Isotactic Polypropylene. *International Journal of Polymer Science* 2016: 1-9.
21. Mulhaupt R, Ovenall DW, Ittel SD, (1988) Control of composition in ethylene copolymerizations using magnesium chloride supported Ziegler-Natta catalysts. *Journal of Polymer Science Part A: Polymer Chemistry* 26(9): 2487-2500.
22. Soga K, Park JR, Shiono T, Kashiwa N (1990) A direct evidence for the improvement of isospecificity Ziegler-Natta catalysts by ethyl benzoate.

- Macromolecular Rapid Communication 11(3): 117-121.
23. Zhou X, Lin S, Chien JCW (1990) Magnesium chloride supported high mileage catalysts for olefin polymerization. XXI. Isospecific and regiospecific vanadium catalyst for propylene polymerization. *Journal of Polymer Science Part A: Polymer Chemistry* 28(10): 2609-2632.
 24. Noristi L, Barbè PC, Baruzzi G, (1991) Effect of the internal/external donor pair in high-yield catalysts for propylene polymerization, 1. Catalyst-cocatalyst interactions. *Makromolekulare Chemie* 192(5): 1115-1127.
 25. Soga K, Ohgizawa M, Shiono T (1993) Copolymerization of ethylene and propene with a $\text{TiCl}_4/\text{MgCl}_2\text{-Al}(\text{C}_2\text{H}_5)_3$ catalyst system using a stopped-flow method. *Makromolekulare Chemie* 194(8): 2173-2181.
 26. Dil EJ, Pourmahdian S, Vatankhah M, Taromi FA (2010) Effect of dealcoholation of support in MgCl_2 -supported Ziegler-Natta catalysts on catalyst activity and polypropylene powder morphology. *Polymer Bulletin* 64(5): 445-457.
 27. Klendworth DD, Reinking MK, Kist ED (2008) Magnesium chloride support.
 28. Invernizzi R, Ligorati F, Fontanesi M, Catenacci R (1983) Supported catalysts for the polymerization of ethylene.
 29. Chadwick JC, van der Sar JC (1988) Preparation of spherical magnesium alkoxide particles.
 30. Jiang T, Chen W, Zhao F, Liu y, Wang R, et al. (2005) Preparation of porous spherical $\text{MgCl}_2/\text{SiO}_2$ complex support as precursor for catalytic propylene polymerization. *Journal of Applied Polymer Science* 98(3): 1296-1299.
 31. Rojanotaikul P, Ayudhya SKN, Charoenchaidet S, Faungnawakij K, Soottitawat A (2012) Preparation of Porous Anhydrous MgCl_2 Particles by Spray Drying Process. *Engineering Journal* 16(3): 109-114.
 32. Abboud M, Denifl P, Reichert KH (2005) Advantages of an Emulsion-Produced Ziegler-Natta Catalyst Over a Conventional Ziegler-Natta Catalyst. *Macromolecular Materials and Engineering* 290(12): 1220-1226.
 33. Spencer MD, O'Reilly N (2014) Emulsion process for improved large spherical Polypropylene catalyst.
 34. Zhidong Z, Main C (2008) Spherical catalyst for olefin polymerization.
 35. Ronkko H, Korpela T, Knuutila H, Pakkanen TT, Denifl P, et al. (2009) Particle growth and fragmentation of solid self-supported Ziegler-Natta-type catalysts in propylene polymerization. *Journal of Molecular Catalysis A: Chemical* 309(1-2): 40-49.
 36. Garoff T, Pesonen K, Waldvogel P, Denifl P, Lindroos J Method for the preparation of olefin polymerization catalysts.
 37. Denifl P, Leinonen T Catalyst particles.
 38. Denifl P, Leinonen T (2007) Process for preparing an olefin polymerization catalyst component.
 39. Singh G, Bantu B, Kaur S (2004) Precursor for catalyst, process for preparing the same and its use thereof.
 40. Boor J (1979) Ziegler-Natta Catalyst Polymerization. 1st(Edn.), Academic Press, New York, pp: 688.
 41. Kaur S, Bantu B, Singh G, et al. (2017) Particle size distribution control through internal donor in Ziegler-Natta catalyst.

